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Methods for the Determination of Trace Organic Materials in Water

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FOREWORD

This is the one hundred and fifty-second of a series of reports designed to present accounts of progress in saline water conversion with the expectation that the exchange of such data will contribute to the long-range development of economical processes applicable to large-scale, low-cost demineralization of sea or other saline water.

Except for minor editing, the data herein are as contained in the reports submitted by Rocketdyne Division of North American Aviation under Contract No. 14-01-0001-332, covering research carried out through May 31, 1965. The data and conclusions given in this report are those of the Contractor and are not necessarily endorsed by the Department of the Interior.

Created in 1849, the Department of the Interior--America's Department of Natural Resources--is concerned with the management, conservation, and development of the Nation's water, wildlife, mineral, forest, and park and recreational resources. It also has major responsibilities for Indian and Territorial affairs.

As the Nation's principal conservation agency, the Department of the Interior works to assure that nonrenewable resources are developed and used wisely, that park and recreational resources are conserved for the future, and that renewable resources make their full contribution to the progress, prosperity, and security of the United States--now and in the future.

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ABSTRACT

The purpose of this research effort was to advance the state-of-the-art in analytical chemistry as it relates to the problem of water desalination. More specifically, studies were conducted to advance instrumental means for organic trace analysis applicable to the quality control of product water, and to the chemical characterization of nonpotable water.

The first phase of the program was concerned with the development of analytical methodology for the detection of organic materials (specifically, hydrocarbons, Freons*, amines, and long-chain alcohols), which come into contact with water as a result of various desalination processes. Techniques based on gas chromatographic separation and ionization detection were developed and successfully utilized for the direct analysis of all four classes of organic compounds at trace levels in the water matrix.

The second phase of this program dealt with the chemical characterization of naturally occurring organic compounds in water sources. To accomplish this, an analytical approach based on separation and preconcentration (by means of vacuum distillation) of the volatile and nonvolatile organic fractions, coupled with removal of the water matrix, was used. The volatile organic fraction was then analyzed gas chromatographically, and the nonvolatile fraction was characterized by a combination of other instrumental techniques.

*Trade name of E. I. du Pont de Nemours & Co., Inc.

INTRODUCTION

The development of analytical methods for the determination of trace organic materials in water has been conducted under the auspices of the Office of Saline Water, U. S. Department of the Interior, since June 1963. The research program consisted of two phases.

The objective of the first phase of the study was to develop an analytical methodology which could be applied to the quality control of product water. The analytical approach was motivated by practical operational needs of desalination plants, which are as follows:

1. Procedural and instrumental simplicity, to permit utilization of developed techniques by nonprofessional personnel
2. Utilization of commercially available instrumentation to reduce capital requirements of desalination plants
3. Desirability of utilizing a common analytical principle for the solution of all problems encountered
4. Adaptability to automation

On the basis of these considerations, a gas chromatographic approach combined with the utilization of highly sensitive ionization detection devices appeared to be best suited to the requirements of this program and was extensively studied.

The second phase of this study was concerned with the development of a means for the chemical characterization of raw (nonpotable) water. The technical requirements of the second phase of this program were different from the first, and the analytical approach was influenced by the following considerations:

1. Complexity and variety of trace organics naturally found in water sources
2. Low concentration level of contaminants

Consequently, attempts were made to: (1) provide a satisfactory means of separation for a complex mixture of organics found in a water matrix, and (2) provide the necessary means of preconcentration to meet the needs for ultrasensitivity of detection.

On the basis of these considerations, an analytical approach based on separation and preconcentration (by means of vacuum distillation) of volatile and nonvolatile organic fractions, coupled with the removal of the water matrix was studied.

EXPERIMENTAL PROGRAM

PHASE 1: METHODS FOR THE DETECTION OF ORGANIC MATERIALS INTRODUCED INTO POTABLE WATER BY DESALINATION PROCESSES

DEFINITION OF THE PROBLEM

The object of all desalination processes is the preparation of potable water from nonpotable water sources. Both physical and chemical treatments of the nonpotable water are employed. Among the physical treatments used are distillation and membrane transport. Chemical treatments involve the utilization of selected chemicals for the purification of nonpotable water. The important methods based on the use of chemicals for water purification currently studied are the direct freezing process, hydrate process, solvent extraction, and electrodialysis.

In the direct freezing process, hydrocarbons are used to reduce the temperature of the feed water with resulting formation of pure ice crystals.

In the hydrate process, hydrocarbons and Freons are used to form gas hydrate compounds with water which are then separated from the brine and subsequently decomposed, producing purified water.

The solvent extraction method uses polar organic compounds (such as amines) to separate the water matrix from its salts.

In all three processes, raw (nonpotable) water comes in direct contact with chemical agents which are subsequently removed by a variety of methods. To guarantee the purity of product water, the amount of residual organics must be closely controlled. A number of analytical methods could be used for the detection of specified organics in a water solution, including colorimetric, electrochemical, spectroscopic, and gas chromatographic techniques. This research effort was devoted to developing gas chromatographic methodology for the following reasons:

1. The technique is both a qualitative and quantitative method of analysis.
2. It provides both selectivity and sensitivity unmatched by other methods. The latter is of prime importance when detection of sub-ppm concentration levels is required.
3. The technique is instrumentally simple and could be utilized by nonprofessional personnel with a minimum of training.
4. Numerous inexpensive instruments are commercially available and could be utilized in desalination plants of all sizes with a minimum of capital investment.
5. The technique can be applied to the analysis of all classes of organic materials which are of interest to desalination technology.
6. Direct analysis of the sample is possible.

INSTRUMENTAL REQUIREMENTS

The following instrumentation was employed during the study.

1. A gas chromatograph manufactured by the Wilkens Instrument and Research Co. with a flame ionization detector and nonlinear temperature programmer

2. A hydrogen generator, Model 650, manufactured by the same company

3. Potentiometric recorder, 1-millivolt full scale, Model SR-20, manufactured by The Sargent Co.

Two different models of gas chromatographs were used. One was Aerograph HyFi Model 600A, and the other was Aerograph HyFi Model 600C. The latter instrument incorporates an electrometer of better quality and demonstrated a considerably higher order of sensitivity than Model 600A. In the technical discussion which follows, the model of the gas chromatograph used will be indicated in all cases where quantitative results are reported. Quantitative data obtained with one instrument cannot be directly related to quantitative data obtained with the other, and, in general, calibration of every instrument used is required.

Because different gas chromatographic instruments, recorders, and sensitivity settings were used during this study, the quantitative data reported are uniformly reduced to the maximum sensitivity of the respective instruments as recorded on a 1-millivolt full-scale recorder.

A number of other gas chromatographic instruments are commercially available, and could be used for the purpose of performing analytical tests described in this report. The recommended requirements for such instrumentation are:

1. Good quality electrometer and recorder
2. Suitable hydrogen flame ionization detector
3. Heated enclosure for the separating column with the capability of being temperature programmed either linearly or nonlinearly.

METHOD DEVELOPMENT

The experimental portion of this phase of the program involved the development of analytical techniques based on gas chromatographic methodology for trace analysis of hydrocarbons, Freons, amines, and alcohols in a water matrix. The effort used to develop the method consisted of two essential parts: (1) optimization of a gas chromatographic technique for the separation of a particular class of compounds, and (2) application of the developed technique to the direct analysis in a water matrix.

ANALYSIS OF HYDROCARBONS IN WATER

Two desalination processes, namely, direct freezing and hydrate, utilize hydrocarbons in direct contact with processed water. The hydrocarbons used are n-butane and propane, and because they are slightly soluble in water (n-butane 61.4 ppm, propane 62.4 ppm), they could remain in the product water. This part of the investigation was directed toward establishing analytical techniques for the separation and detection of these two hydrocarbons, plus hydrocarbons which are present as impurities in technical-grade butane and propane.

The first part of the study dealt with the development of efficient techniques for gas chromatographic separation of a broad boiling range of hydrocarbons. The second part of this effort was directed toward the detection and analysis of trace hydrocarbons in water, using a direct gas chromatographic technique, and quantification of procedures.

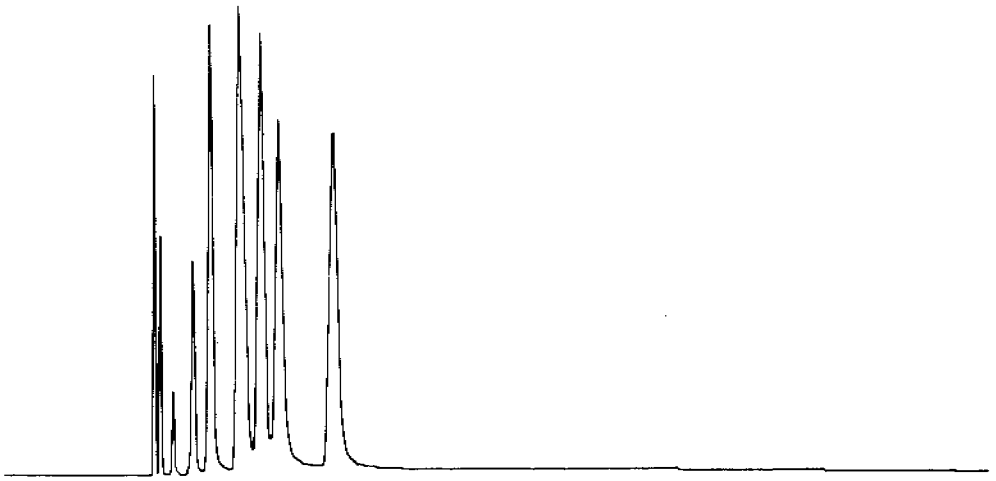
Separation

A single gas chromatographic substrate capable of separating a broad range of hydrocarbons (from gases to high-boiling materials) would be best suited. However, in the initial stages of this study, such columns were not available. Therefore, separate investigations were conducted on the separation of two ranges of hydrocarbons, i.e , C_1 to C_5 and C_5 to C_{16}. The separation of C_1 to C_5 hydrocarbons has been successfully demonstrated by a number of investigators (Ref. 1 and 2) using a separating column of dimethylsulfolane (2, 4-dimethylthiophene-1, 1-dioxide) as the column substrate with thermoconductivity detection. This approach, therefore, was a logical choice for the initial study. However, to provide increased sensitivity of detection for hydrocarbons in a water matrix, and relative insensitivity to the matrix itself, it was decided to utilize hydrogen flame ionization detection.

A number of 1/8-inch-OD columns containing dimethylsulfolane substrate, differing in length and loading of the liquid phase, was investigated. The best results were obtained by the use of a 36-foot column of Chromosorb W coated with 20-percent (w/w) dimethylsulfolane. As shown in Fig. 1, the separation of most of the C_1 to C_4 hydrocarbons (including cis- and trans-butene-2) was achieved. The 0.02-cc gas samples were injected by means of a multiport injection valve in conjunction with a stream-splitting device. Using flame ionization detection, no base line drift that might be expected from the relatively high vapor pressure of dimethylsulfolane was observed.

A detailed description of this procedure is presented in the annual report (1964) under the subject contract (Ref. 3), and specific conditions of the optimized procedure are presented in Fig. 1.

The analysis of higher hydrocarbons using flame ionization detection is hampered by a minute bleeding of the stationary liquid phase at higher



	Conditions
Instrument:	Aerograph HyFi, Model 600A
Detector:	Flame Ionization, H_2 flow, 20 cc/min; air flow, 250 cc/min.
Column:	36-foot long, 1/8-inch diameter 20 percent 2,4-dimethyl-sulfolane on 30-60 mesh chromosorb.
Sample:	0.2-cc gas--mixture of natural gas and Phillips 66 hydrocarbon mixture No. 37, split 1:10
Carrier Gas:	Argon, inlet pressure 30 psig, rate of column flow—25 cc/min.
Temperature:	35° C
Sensitivity:	$8 \times 10^7 \times 1$
Recorder Speed:	1/2 in./min

Peaks in order of elution

1. Methane
2. Ethane
3. Propane
4. iso-Butane
5. n-Butane
6. Butene - 1 + Isobutylene
7. trans-Butene - 2
8. cis-Butene - 2
9. Butadiene - 1,3

Figure 1. Separation of C_1 to C_4 Saturated and Unsaturated Hydrocarbons

temperatures. Such bleeding is rarely observed using a thermoconductivity detector, because of the relatively low sensitivity of such a device; however, when higher sensitivity detection devices are used (such as hydrogen flame ionization) bleeding of the substrate at higher temperatures becomes a major problem.

The use of coated glass beads circumvents this problem by permitting separation at temperatures appreciably below the boiling point of the analyzed compound. For this reason, it was decided to investigate this technique as a means of separation of the C_5 to C_{16} hydrocarbons.

The conventional way to prepare a coated glass bead column has been by dissolving the liquid phase in a volatile solvent, mixing it with the glass beads, and drying it (Ref. 4). Utilizing such a technique, a number of difficulties were encountered, particularly nonuniformity in liquid deposit on the beads.

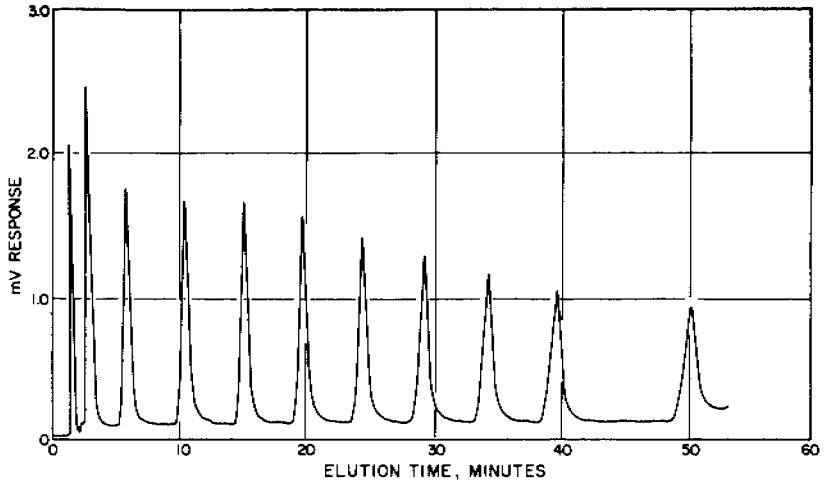
Attempts were made to deposit the substrate in a column already packed with dry glass beads, by first saturating the column with a solution of the substrate, and removing the solvent by application of a slight vacuum across the column. This technique was found to be unsatisfactory because the solvent, while being removed, tends to redissolve the substrate and redeposit it nonuniformly throughout the column.

To overcome this difficulty, a technique of dynamic deposition of the substrate was developed. With this technique, a vacuum is applied alternately to the head and tail of the column, providing a flux of substrate in both directions while removing the solvent. A column prepared in the manner described provided separation of all C_5 to C_{16} alkanes by carbon number group. Detailed descriptions of this procedure appear in Ref. 3 and 5. A gas chromatographic separation of C_5 to C_{16} alkanes and optimized operating conditions are shown in Fig. 2.

Zhdanoff, et al. (Ref. 6) used porous glass (300 Å pore size) for the separation of hexane, heptane, octane, nonane, and decane under isothermal conditions. They also separated benzene, toluene, ethylbenzene and isopropylbenzene using porous glass of approximately a 50 Å pore size.

MacDonnell, et al. (Ref. 7) separated materials such as carbon tetrachloride and pentane using Corning Glass Co. porous glass Code 7930. These two investigations greatly extended the use of the gas-solid chromatographic principle, making separation and analysis of higher boiling liquids on a solid support possible without the use of a liquid phase. The inherent superiority of gas-solid chromatography when used in conjunction with a highly sensitive means of detection is apparent. Because no stationary liquid phase is present in the column, no column bleeding effects would be detected by the detector.

An evaluation of porous glass as a gas chromatographic separating media was then undertaken. The results of this investigation have been reported (Ref. 3 and 8) and are summarized as follows.



Conditions		Peaks in order of elution		
Instrument:	Aerograph HyFi, Model 600A	1.	iso-C_5H_{12}	35°C
Detector:	Flame Ionization, H_2 flow, 20 cc/min; air flow, 250 cc/min.	2.	n-C_6H_{14}	35°C
		3.	n-C_7H_{16}	40°C
Column:	10-foot long, 1/8-inch diameter; dynamically loaded with Apiezon T on 60-80 mesh glass beads	4.	n-C_8H_{18}	65°C
		5.	n-C_9H_{20}	90°C
Sample:	Mixture of C_5 to C_{16} hydrocarbons, 1 µl.	6.	n-$C_{10}H_{22}$	110°C
		7.	n-$C_{11}H_{24}$	130°C
Carrier Gas:	Argon, inlet pressure 5 psig; rate of flow, 20 cc/min.	8.	n-$C_{12}H_{26}$	150°C
		9.	n-$C_{13}H_{28}$	165°C
Temperature:	Programmed from 30° to 225°C at 75 percent power	10.	n-$C_{14}H_{30}$	180°C
		11.	n-$C_{16}H_{34}$	215°C
Sensitivity:	10^7 x 4 x 1			
Recorder Speed:	0.2 in./min.			

Figure 2. Separation of C_5 to C_{16} Saturated Hydrocarbons

Porous glass plates were procured from Corning Glass Co., appropriately ground, and used for the preparation of a gas chromatographic column. The pore diameter of this glass was 40 Å. A 10-foot-long, 1/8-inch-diameter stainless-steel column packed with untreated porous glass (50-80 mesh) was used for separating methane, ethane, propane, iso-butane, n-butane, butene-1, and butene-2.

For the separation of higher hydrocarbons, experiments were conducted using multiple 10-foot lengths of 1/8-inch-diameter column packed with porous glass (30-50 mesh). Several columns were combined in series and tested in lengths of 30, 20, and 10 feet, for the separation of C_1 to C_{16} hydrocarbons under programmed temperature conditions. The best results were obtained with a 10-foot-long column under the following conditions:

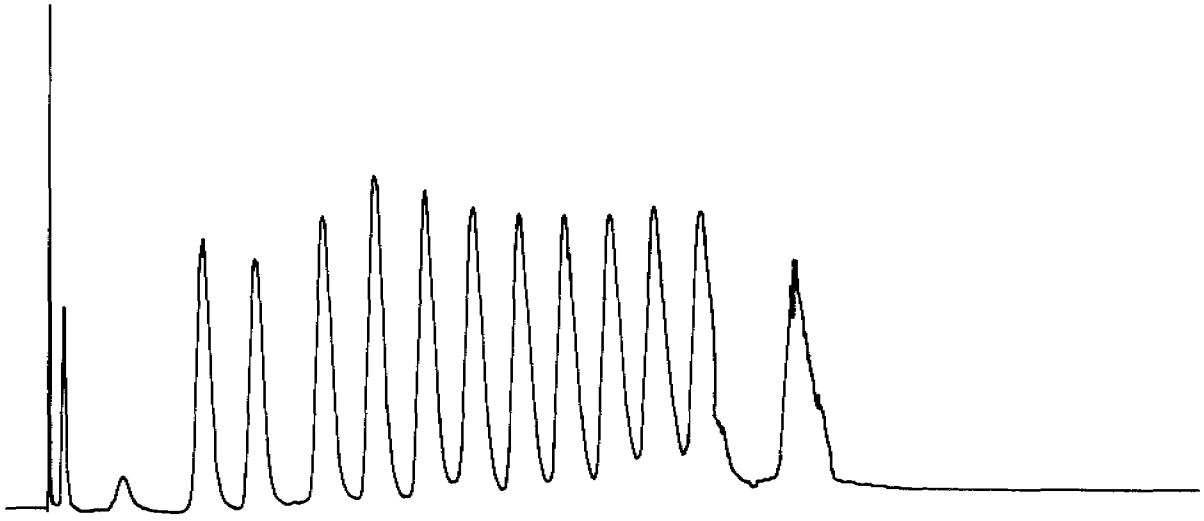
Instrument:	Aerograph HyFi Model 600A
Detector:	Flame Ionization, hydrogen flow, 25 cc/min; air flow, 250 cc/min
Column:	10-foot-long, 1/8-inch-diameter stainless-steel tube packed with Corning Glass Co. porous glass No. 7930; 30-50 mesh size; average pore diameter 40 Å
Sample:	0.2-cc natural gas and 2.5 microliters of a prepared mixture of C_5 to C_{16} hydrocarbons injected simultaneously; split 1:5
Carrier Gas:	Argon, inlet pressure 20 psig, rate of flow, 30 cc/min
Temperature:	Programmed from 5° to 325°C
Sensitivity:	$4 \times 10^7 \times 1$
Recorder Speed:	0.2 in./min

Simultaneous injection of both gas and liquid samples was necessary to obtain a representative hydrocarbon mixture in the C_1 to C_{16} range. No hydrocarbon of the C_{15} group was available but examination of the gas chromatogram (Fig. 3) showed a void space where it should appear. The order of elution and approximate temperatures at which the peaks appeared are shown in Fig. 3.

By increasing the length of the column and adjusting the temperature program according to the requirements of the specific analysis, even more complete resolution of the hydrocarbon isomers appears possible.

The experimental results indicated great usefulness of porous glass as a gas chromatographic separating medium, especially in conjunction with flame ionization detection and temperature programming.

The developed analytical technique for the separation of a broad range of hydrocarbons using porous glass offers numerous advantages over the gas-liquid chromatographic separations, and, for those reasons, it was decided



Conditions	
Instrument:	Aerograph HyFi Model 600A
Detector:	Flame Ionization, H_2 flow, 25 cc/min; air flow, 250 cc/min.
Column:	10-foot long, 1/8-inch-diameter stainless-steel tube packed with Corning Co. porous glass No. 7930; 30-50 mesh size; average pore diameter 40 A
Sample:	0.2-cc natural gas and 2.5 microliters of a prepared mixture of C_5 to C_{16} hydrocarbons injected simultaneously; split 1:5
Carrier Gas:	Argon, inlet pressure 20 psig, rate of flow 30 cc/min
Temperature:	Programmed from 5°to 325°C
Sensitivity:	$4 \times 10^7 \times 1$
Recorder Speed:	0.2 in./min

Peaks in order of elution

1. CH_4, 5°C
2. C_2H_6, 10°C
3. n-C_3H_8, 35°C
4. n-C_4H_{10}, 70°C
5. iso-C_5H_{12}, 100°C
6. n-C_6H_{14}, 145°C
7. n-C_7H_{16}, 170°C
8. n-C_8H_{18}, 195°C
9. n-C_9H_{20}, 210°C
10. n-$C_{10}H_{22}$, 230°C
11. n-$C_{11}H_{24}$, 245°C
12. n-$C_{12}H_{26}$, 260°C
13. n-$C_{13}H_{28}$, 270°C
14. n-$C_{14}H_{30}$, 285°C
15. n-$C_{16}H_{34}$, 305°C

Figure 3. Separation of C_1 to C_{16} Saturated Hydrocarbons

to use this technique as the basis for the analytical procedure for the detection of trace hydrocarbons in water.

Determination of Hydrocarbons in a Water Matrix

Conventional analytical procedures for the determination of organic materials in water involve the separation and preconcentration of solute from solvent. The separation and preconcentration can be accomplished in many ways, such as adsorption of organic matter on activated charcoal (Ref. 9), extraction with organic solvents (Ref. 10), or gas stripping (Ref. 11). The object of this investigation was to devise an analytical procedure which would permit direct detection of organics in water, without a separation and preconcentration step.

To facilitate such a procedure, gas chromatographic separation on a porous glass substrate was combined with flame ionization detection of the eluted organic fractions. Because the hydrogen flame ionization detector plays a major role in this scheme, its characteristics and mode of operation will be discussed briefly in the following paragraphs. The response of a flame ionization detector to a great number of organic materials has been studied very extensively by a number of investigators (Ref. 12 through 14).

The work of Rouayheb (Ref. 12) indicates that the response of a flame ionization detector, which is expressed as relative area/mole, is linear and proportional to the carbon number of a homologous series of organic compounds. Different curves were reported for the response of alcohols, organic acids, esters, amines, and nitriles, but in all cases, the relative area per mole is proportional to the carbon number.

Because this phase of the program dealt with homologous series of saturated hydrocarbons, standardization of the instrument response to particular hydrocarbons was unnecessary. The response of the instrument to a mixture of hydrocarbons was assumed to be proportional to the weight percent concentration of individual components, because mole concentration divided by carbon number in a saturated hydrocarbon series is approximately proportional to weight percent.

The mechanism of operation of the flame ionization detector involves the combustion of organic matter in a hydrogen-oxygen flame. The combustion products are carbon dioxide and water. Because water is always present in the hydrogen-oxygen flame, it was assumed that the addition of water which was eluted from the column would not affect the response of the instrument. This was found to be true when the readout system was operated at low sensitivities. However, during the course of this study, it was necessary to use maximum instrumental sensitivity, and then it would found that water vapor eluted from a column does affect the response of the hydrogen flame ionization detector. The mechanism of such a response is not clear at this time, but might be caused by the changes in density and flow characteristics of the carrier gas at the time interval when the water vapor reaches the detection head.

The water sample, when injected into the gas chromatograph and separated on the porous glass column, produces a characteristic tailing peak which appears in the region of elution of C_9-C_{14} hydrocarbons. Using standard solutions of hydrocarbons in water, it was possible to calculate that the response of the hydrogen flame ionization detector to water vapor is approximately 10^{-5} to 10^{-6} that of organic matter. The water peak is easily recognizable by its shape. Hydrocarbons in the overlap region appear as sharp peaks on the water tail. Therefore, they are measured from the water tail and not the baseline.

Once the possibility of direct gas chromatographic analysis for hydrocarbons in water was established, an attempt was made to quantify the procedure and establish the lower limit of detection.

Because of very low solubility, a number of difficulties was encountered in preparing standard solutions of alkanes in water, and it was decided to use a solution of benzene in water for calibration of the procedure. The solubility of benzene in water is quite high (1780 ppm) and it was possible to prepare (using a dilution technique) standard solutions in water containing 11, 44, 88, 440, and 880 ppb of benzene. This solution was analyzed under the following set of conditions.

Instrument:	Wilkens Aerograph HyFi Model 600C
Detector:	Hydrogen flame ionization; hydrogen flow, 25 cc/min; air flow, 250 cc/min
Column:	1-foot-long, 3/16-inch-diameter stainless-steel tube, packed with Corning Glass Co. porous glass No. 7930; 80-10 mesh size, average pore diameter, 40 Å
Column Temperature:	115°C isothermal
Carrier Gas:	Purified helium, flowrate, 25 cc/min
Sample:	25 μl aliquots of various benzene concentrations (11 to 880 ppb) in water
Sensitivity:	1 x 4
Recorder:	Sargent, 0 to 1 millivolt full scale

Benzene was eluted in the form of a sharp peak and for this reason calibration could be accomplished using peak height rather than area measurement. The results are reported in Table 1.

The calibration for benzene in water is shown in Fig. 4, and indicates that determination of hydrocarbons in a water matrix is possible to 10 parts per billion, using the experimental technique and instrumental setup described.

Recommended Method for the Analysis of Hydrocarbons in Water

Based on the experimental work described, the following direct gas chromatographic procedure is recommended for trace analysis of hydrocarbons in water.

TABLE 1

CALIBRATION OF HYDROGEN FLAME IONIZATION DETECTOR RESPONSE WITH SOLUTION OF BENZENE IN WATER (25 μl SAMPLE SIZE)

Benzene Concentration, ppb	Peak Height, millimeters
0	1.0
11	2.2
44	6.5
88	11.5
440	56.0
880	104.0

Sensitivity: 14 millimeters per 100-ppb benzene

Instrumental Requirements. A suitable temperature-programmed gas chromatograph with a hydrogen flame ionization detector, electrometer, and potentiometric recorder is required as well as a 10-foot-long, 1/8-inch-diameter gas chromatographic column made of a stainless-steel tube. The column is packed with 30-50 mesh size, average pore diameter 40 Å Corning Glass Co. porous glass No. 7930. The glass is available from Corning Glass Co. in the form of plates, rods, and sieved powder.

Procedure. A gas chromatograph fitted with the previously described column is operated under the following set of conditions:

Detector:	Hydrogen flame ionization; hydrogen flow, 25 cc/min; air flow, 250 cc/min
Temperature:	Programmed from 20° to 350°C
Sample:	Water 25 μl

A sample of water is injected into the gas chromatograph at room temperature, and the temperature is programmed to increase at 5°C/min. The peaks of C_1 to approximately C_8 hydrocarbons appear prior to the elution peak for water. The peaks of C_9 to approximately C_{14} hydrocarbons will appear as sharp peaks on the water tail. Higher hydrocarbons will appear on the gas chromatogram as sharp peaks similar to the peak eluted prior to the water peak.

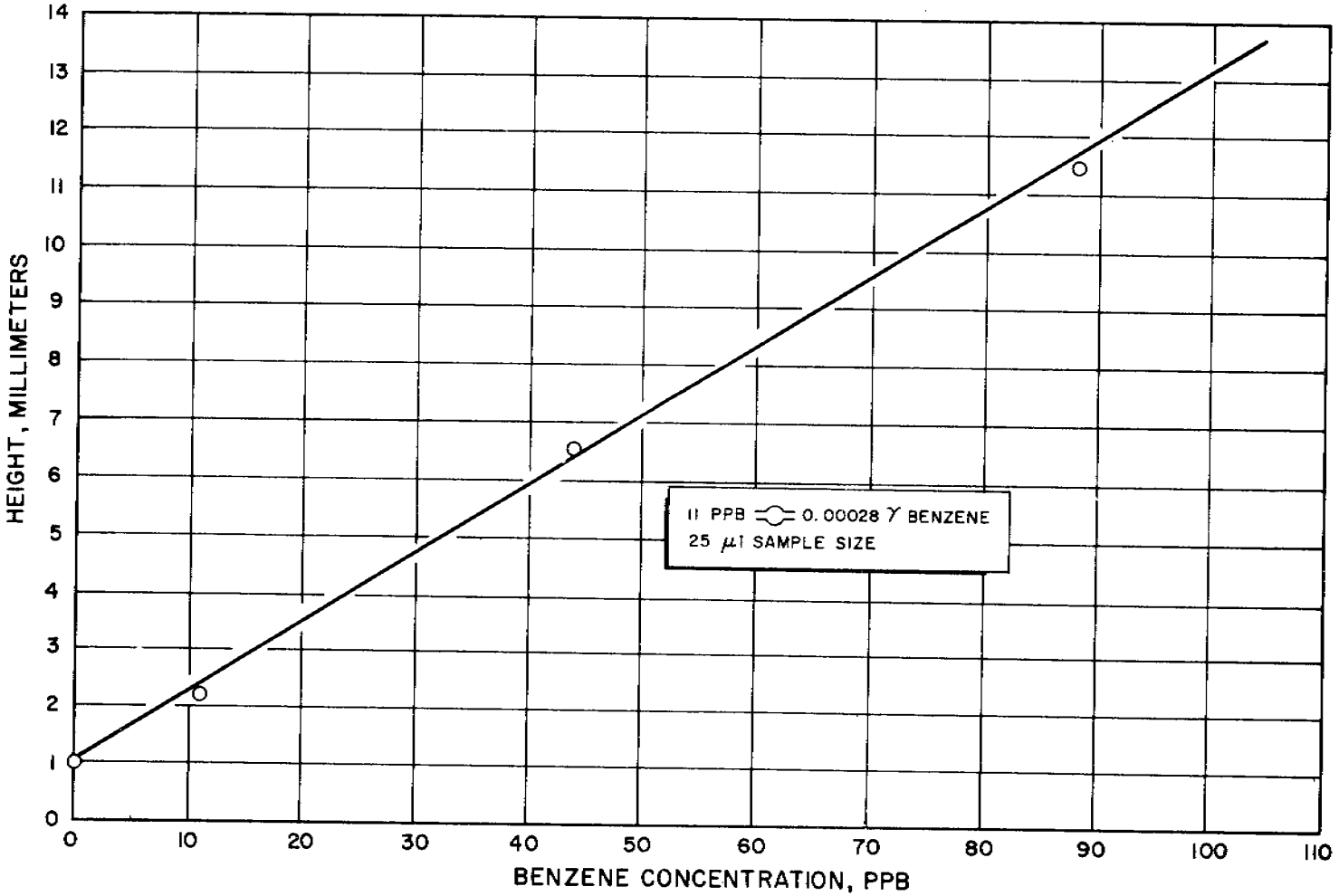


Figure 4. Calibration of Flame Ionization Detector With Benzene

Calibration. To permit quantitative analysis of dissolved hydrocarbons in water, calibration of the procedure is necessary using appropriate standards of benzene in water.

Calculations. The peak area corresponding to 1-ppm benzene is calculated. The concentration of the specified hydrocarbon is then calculated according to the following formula:

$$\text{ppm hydrocarbon found} = \frac{\text{area } (\text{cm}^2) \text{ of the hydrocarbon peak}}{\text{area } (\text{cm}^2) \text{ of 1-ppm benzene peak}}$$

Sensitivity. The lowest limit of detection experimentally demonstrated using benzene is 10 ppb.

ANALYSIS OF FREONS IN WATER

The fluorocarbons (Freons) have shown a potential as coolants in freezing processes, and also demonstrated the ability to form gas hydrates with water. Hence, their potential use in practical desalination processes can be anticipated, and methods for their qualitative and quantitative analysis at trace levels in a water matrix will be required. The experimental phase of the study was divided into two parts: separation and detection in a water matrix.

Separation

The monophase gel (Kel-F) column (Ref. 15) provides an excellent means for the separation of the majority of Freons. Unfortunately, the monophase substrate cannot be used at temperatures above 60° to 70°C because of column bleeding. Numerous other gas-liquid chromatographic columns suffer from the same shortcoming, and, for this reason, developmental effort was divided toward further evaluation and application of porous glass as a separating media.

A representative number of Freons covering a broad boiling range was chosen for this study. The following materials were investigated:

1. Freon 13, chlorotrifluoromethane, $ClCF_3$
2. Freon 22, chlorodifluoromethane, $HClCF_2$
3. Freon 12, dichlorodifluoromethane, Cl_2CF_2
4. Genetron-1132A, 1,1-difluoroethylene, $F_2C_2H_2$
5. Genetron-21, dichlorofluoromethane, Cl_2CFH
6. Freon 11, trichlorofluoromethane, Cl_3CF

The lowest boiling member of the series is Genetron-1132A boiling at -83°C and the highest boiling member is Freon 11 boiling at 24°C.

During the experimental part of this study, two gas chromatographs were used: (1) a custom-built instrument with a thermoconductivity detector was used in the initial experiments to establish the feasibility of Freon separation on porous glass, and (2) later a Wilkens HyFi gas chromatograph with flame ionization detection was used to complete the study.

The separation of Freons on a porous glass column was carried out using both temperature programming and isothermal conditions. The gas chromatogram for Freons separated under temperature-programmed conditions using custom-built instruments is shown in Fig. 5. The instrument operating conditions and retention times are also reported in the same figure. It was also established that these Freons could be separated isothermally at 100°C, with retention times reported in Table 2. In the latter part of the investigation, Freons were separated on a 6-foot-long, 1/8-inch-diameter porous glass column using a Wilkens HyFi gas chromatograph with flame ionization detection. The gas chromatogram of this separation is shown in Fig. 6 where operating conditions are also reported. Examination of the figure indicates that sharper peaks are obtained than in previous experiments using a thermoconductivity detector. This is probably caused by the smaller sample sizes used and the smaller diameter of the separating column.

These initial experiments demonstrated that porous glass is a satisfactory column material for the gas chromatographic separation of Freons boiling over a wide range.

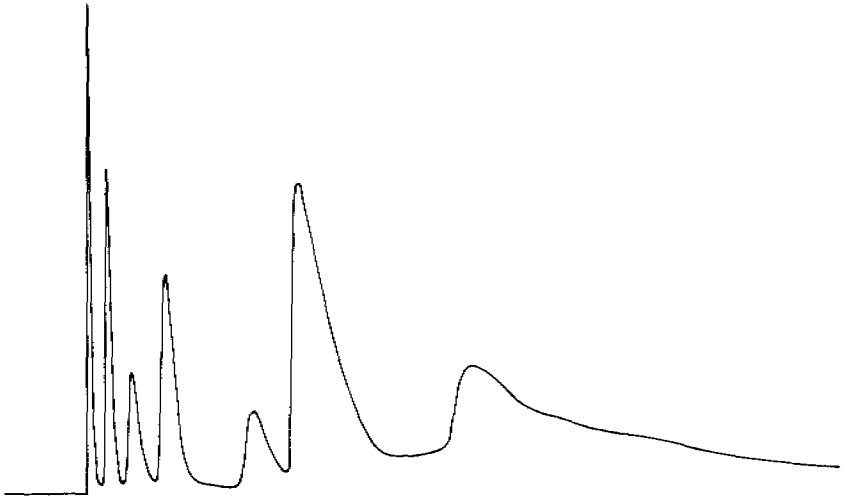
TABLE 2

RETENTION TIMES FOR FREONS AT 100°C

Freon	Boiling Point, °C	Retention Time,	
		Minutes	Seconds
Chlorotrifluoromethane	-81.4	1	15
1,1-Difluoroethylene	-83	1	50
Dichlorodifluoromethane	-29.8	2	30
Chlorodifluoromethane	-40.8	4	30
Trichlorofluoromethane	23.8	6	30
Dichlorofluoromethane	8.9	11	30

Determination of Freons in a Water Matrix

The extreme sensitivity and specificity of an electron capture detector to the compounds containing electronegative groups make it a highly attractive choice for the analysis of Freons. The initial experiments dealing with the determination of Freons in a water matrix were made using an electron capture detector in combination with the separation on a porous glass column. It was immediately established that a water matrix affects this type of detection adversely and must be removed or prevented in some way from reaching the detector.

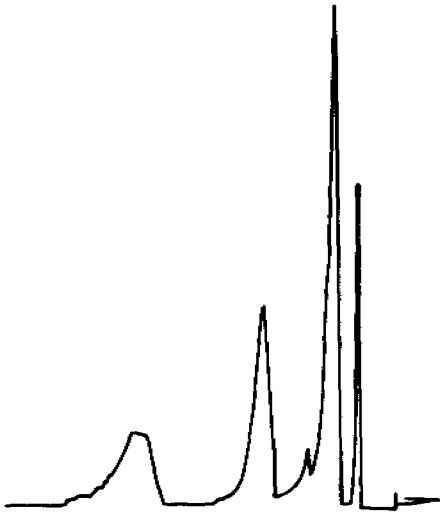


Conditions	
Instrument:	Custom built gas chromatograph temperature programmed
Detector:	Gow-Mac temperature controlled cell, Model TR-III-A TH temperature, 25°C
Column:	10-foot long, 3/16-inch diameter packed with 50-80 mesh size Corning Co. porous glass No. 7930
Carrier Gas:	Helium, inlet pressure 20 psig rate of flow 40 cc/min.
Temperature:	Column programmed from 90° to 150°C
Sensitivity:	4
Recorder:	Leeds & Northrup, Model G, 1 mV full scale, speed, 1/2 in./min
Sample:	Mixture of 5 Freons 1cc gas; and 5 µl of Freon 11 liquid

Peaks in order of elution

	Boiling point	Retention time
Chlorotrifluoromethane	-81.4°C	1' 30"
1,1 -Difluoroethylene	-83.0°C	2' 30"
Dichlorodifluoromethane	-29.8°C	3' 30"
Chlorodifluoromethane	-40.0°C	6' 25"
Trichlorofluoromethane	+23.8°C	8' 05"
Dichlorofluoromethane	+8.9°C	14' 0"

Figure 5. Separation of Freons



Conditions		Peaks in order of elution
Instrument:	Aerograph HyFi, Model 600 C	Chlorotrifluoromethane
Detector:	Flame Ionization, H_2 flow, 20 cc/min; air flow, 250 cc/min.	1,1-Difluoroethylene
Columns:	6-foot long, 1/8-inch diameter packed with Corning porous glass No. 7930, 50-80 mesh size.	Dichlorodifluoromethane
Sample:	Mixture of Freons. Sample size 40 microliters.	Chlorodifluoromethane
Carrier Gas:	Nitrogen gas. Inlet pressure 12.5 psig.	
Temperature:	50° C isothermal	
Sensitivity:	Varied	
Recorder:	Varian, 9 mV full scale response, speed 2.5 minutes per inch.	

Figure 6. Separation of Freon Mixture

A number of techniques for water removal, based on chemical and physical principles, was investigated. It was established that while such removal of water is possible, it is rather cumbersome and not practical. Therefore, it was decided to investigate a different approach to this problem.

Because of its high polarity and boiling point, water would be retained on a porous glass column for a considerably longer time than Freons. It could probably be eluted by rapid temperature programming after exit of the highest boiling Freon. To test this assumption, the following experiment was conducted. A water sample (10 μl) was injected into a custom-built chromatograph at a column temperature of 100°C. The instrument was maintained at 100°C for 13 minutes, after which time all the Freons should have been eluted. Thereafter, the temperature program was started at 100-percent power, and the column temperature rapidly reached 200°C. Soon after the start of the temperature program (1 to 2 minutes), the water began to elute.

Because the retention time for water is longer than for the Freons, an analysis could be performed by use of isothermal or programmed-temperature chromatography, which would permit elution of Freons prior to elution of the water peak.

It was initially planned to use an electron capture detector for this analysis and make provisions for the diversion of water vapor from the detector at the predetermined time of elution of the subsequent peak. This approach, while capable of providing the highest possible sensitivity for the detection of Freons, was not pursued because of the necessity of substantial instrumental modification. To be consistent with the stated goals of this study, use of unmodified commercial equipment with simple and straightforward procedural steps must form a basis for the required analytical methodology.

In the course of this study, it was found that Freons respond to flame ionization detection to a satisfactory degree. Therefore, it was decided to recommend an analytical method for their detection similar in instrumentation, operating conditions, and procedural requirements as the one described for the detection of hydrocarbons in water.

Recommended Procedure for the Determination of Freons in Water

Based on the experimental work described, a direct gas chromatographic procedure is recommended for the trace analysis of Freons in water.

Instrumental Requirements. The instrumental requirements are the same as for the determination of hydrocarbons in water.

Procedure. The procedure is in essence the same as described for the detection of hydrocarbons in water, except that the instrument is operated isothermally at 100°C. After sample injection, the peaks for Freons will appear, followed by a broad peak for water.

Calibration. During this study, it was found extremely difficult to prepare an accurate standard solution of Freons in water because of their low solubility. For this reason, it is recommended that calibration be accomplished by injecting known volumes of Freons by means of a gas-tight microsyringe. The integrated areas of the peaks are plotted vs quantities of Freons expressed in micrograms.

Calculation. The integrated area for the Freon peak obtained from an unknown water solution is related to the calibration curve, and the quantity (in micrograms) of the Freon present is established. From this number and the volume of the water sample, the concentration of Freon in water (as ppb) is calculated.

Sensitivity. The sensitivity of the analytical procedure for the detection of Freons in water will approach that of hydrocarbons (10 ppb).

ANALYSIS OF ALCOHOLS IN WATER

High molecular weight alcohols have been used as evaporation suppressors. Cetyl alcohol appears to be the leading candidate for this purpose, and residual solubility of the material in potable water is of importance. The objective of this study was to develop a technique for the analysis of cetyl alcohol in a water matrix at the ppb concentration level. As in other tasks, the study was divided into two parts: gas chromatographic separation, and detection in a water matrix.

Separation

In the initial stage of the study, porous glass was used as the separating substrate for the analysis of alcohols, but it was soon discovered that, because of the high polarity of this material, alcohols at normal operating temperatures were totally retained on a column. The modified porous glass, as described later in this report, was then tried as the separating material, and although low molecular weight alcohols were eluted successfully on such a column, cetyl alcohol remained irreversibly adsorbed even at very high temperatures (350°C).

The indications were that a considerably more extensive study on the nature of adsorption and separation phenomena on porous glass was required before the technology for separation of polar compounds on this substrate could be developed. Therefore, to resolve the immediate problem, conventional gas-chromatographic methodology was used for the separation and detection of alcohols. A column containing 20-percent Carbowax 20M and

10-percent KOH on Chromosorb W (Ref. 16) was prepared and used for the separation of alcohols under the following set of conditions:

Instrument:	Aerograph HyFi Model 600A
Detector:	Flame ionization; hydrogen flow, 30 cc/min; air flow, 250 cc/min
Column:	3-foot long by 1/8-inch diameter packed with 20-percent Carbowax 20 M and 10-percent KOH on 80-100 mesh Chromosorb W
Carrier Gas:	Nitrogen, 10-psig inlet pressure
Sample:	Mixture of C_1, C_2, C_4, C_6, C_8, C_{10}, C_{14}, C_{16}, straight chain alcohols; 3 μl sample size
Sensitivity:	16 x 10
Recorder:	L&N Speedomax, 1-millivolt full-scale response; speed, 1/2 in./min
Temperature:	Temperature programmed from 35°to 230°C

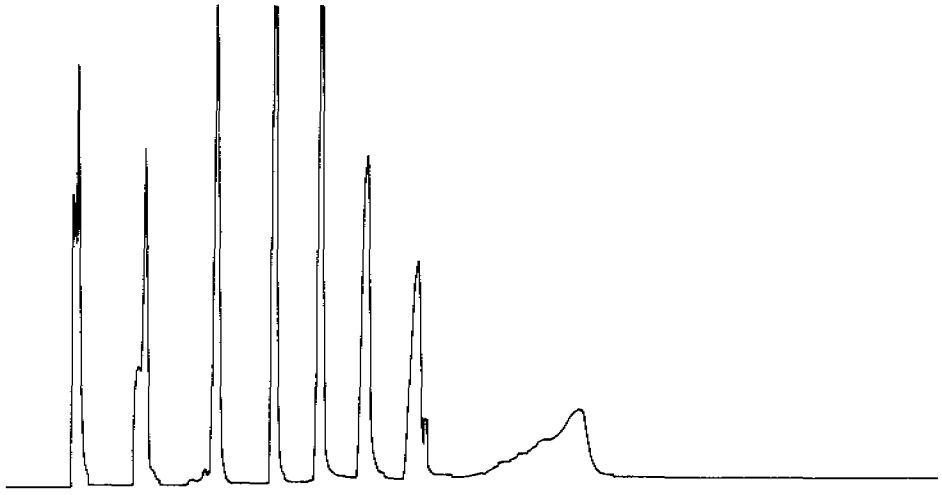
The separation of alcohols accomplished under the above set of conditions was quite satisfactory as shown in Fig. 7. The retention times and temperatures of elution are shown in Table 3.

Determination of Cetyl Alcohol in a Water Matrix

Once the gas chromatograph conditions for alcohol separation were established, an attempt was made to detect cetyl alcohol at trace concentration levels in a water matrix. To prepare a standard 100-ppm solution of cetyl alcohol, a solvent of 70-percent water and 30-percent isopropyl alcohol was required because of the limited solubility of cetyl alcohol in water. The mixture was analyzed under conditions essentially as reported above, except that the starting column temperature was in the 110°to 120°C region. The column was maintained at this temperature until the mixed solvent was completely eluted, and then the temperature program was applied at 100-percent power. The cetyl alcohol peak appeared at approximately 220°to 230°C. While this peak was easily detectable, extensive baseline noise prevented the necessary increase in the sensitivity for detection of lower concentrations.

The reason for this was the low sensitivity of the gas chromatograph used in this study.

Therefore, it was decided to investigate and develop a technique of multiple injection, which would permit parking the cetyl alcohol at the head of the column at lower temperatures while the sample matrix is removed. After a sufficient quantity of sample is accumulated in the column, elution of cetyl alcohol by means of a temperature program, and detection by means of flame ionization would be possible.



Conditions	
Instrument:	Aerograph HyFi Model 600A
Detector:	Flame Ionization H_2 flow, 30 cc/min; air flow, 250 cc/min.
Column:	3-foot long, 1/8-inch diameter packed with 10-percent KOH and 20-percent Carbowax 20M on 80-100 mesh Chromosorb W acid washed.
Sample:	3 microliters of mixed alcohols.
Carrier Gas:	Nitrogen, inlet pressure 10 psig.
Temperature:	Programmed from 35° to 230° C
Sensitivity:	10 x 16 attenuation.
Recorder:	Leeds & Northrup Speedomax, 1 mV full scale response, 0.5 in./min. chart speed.

Peaks in order of elution

Component	Time	Temperature
CH_3OH	0.8'	35° C
C_2H_5OH	1.0'	35° C
i-C_3H_7OH	3.2'	70° C
n-C_4H_9OH	3.6'	75° C
n-$C_6H_{13}OH$	7'	115° C
n-$C_8H_{17}OH$	9'	140° C
n-$C_{10}H_{21}OH$	11'	165° C
n-$C_{12}H_{25}OH$	13'	185° C
n-$C_{14}H_{29}OH$	15'	195° C
n-$C_{16}H_{33}OH$	21'	200° C

Figure 7. Separation of C_1 to C_{16} Alcohols

TABLE 3

SEPARATION OF ALCOHOLS

Alcohol*	Retention Time, minutes	Temperature of Elution, °C**
C_1	1	35
C_2	1	35
C_4	4	75
C_6	7	115
C_8	9	140
C_{10}	12	165
C_{12}	14	185
C_{14}	16	195
C_{16}	22	200

*Straight chain
**Temperature reported as they appear on a thermometer in gas chromatographic oven; actual column temperature could be lower

A series of water-isopropyl alcohol samples containing various concentrations of cetyl alcohol were injected into the gas chromatograph at 2-minute intervals. The instrument was kept at 110°C with a nitrogen inlet pressure of 25 psig. After all of the water and isopropanol were eluted and the baseline had stabilized, the inlet pressure was dropped to 10 psig and the temperature program was started at 100-percent power. A peak for cetyl alcohol appeared at approximately 230°C, as measured by a thermometer in the gas chromatographic oven.

These data reported in Table 4 indicate that sub-ppm concentrations of C_{16} alcohol in a water matrix can be detected using conventional gas chromatographic column separation. It is believed that a considerable increase in sensitivity could be obtained using the improved electrometer of the Model 600-C chromatograph.

The accuracy of the method was rather low because the gas chromatograph (Aerograph HyFi 600A) used in the study was of low sensitivity and required large numbers of injections. The results obtained later with an improved gas chromatograph (Model 600C) indicate that further increase in the sensitivity to organic matter can be obtained. Consequently the recommended procedure could be carried out with considerably fewer injections, which, in effect, will improve the accuracy.

TABLE 4

DETECTION OF CETYL ALCOHOL IN A WATER MATRIX

Concentration of C_{16} Alcohol, ppm	Sample Size, µl*	Micrograms of C_{16} Alcohol	Instrument Response, cm^2	Response (cm^2) per 1 Microgram of C_{16} Alcohol
0.5	2000	1.0	136	136
0.5	3000	1.5	80	53
1.0	1000	1.0	58	58
1.0	1500	1.5	260	173
10.0	200	2.0	424	212
10.0	300	3.0	252	84
10.0	400	4.0	728	182

*Multiple injection

NOTE: Responses have been corrected to maximum sensitivity; the Wilkens HyFi 600A gas chromatograph was used.

Average Response per 1 microgram of cetyl alcohol	128 cm^2
Standard Deviation	±64

Recommended Procedure for the Determination of Cetyl Alcohol in Water

Based on the experimental work described, the following direct gas chromatographic procedure is recommended for the trace analysis of cetyl alcohol in water.

Instrumental Requirements. The basic instrumental requirements are the same as described for the determination of hydrocarbons. The recommended column for this analysis is a 3-foot-long, 1/8-inch-diameter, stainless-steel tube, packed with 20-percent Carbowax 20M and 10-percent KOH on 80-100 mesh Chromosorb W.

Procedure. The gas chromatograph fitted with the column as described above is operated under the following set of conditions:

Detector:	Hydrogen flame ionization; hydrogen flow, 25 cc/min; air flow, 250 cc/min
Temperature:	Isothermal during the injection period at 110°C; after injection of a suitable number of samples, programmed to 230°C at maximum temperature rate
Sample:	100 µl repeatedly injected

A number of water samples are injected repeatedly into the gas chromatograph operated at 110°C. The exact number of injections depends on the concentration of cetyl alcohol in the water.

After completion of the injection cycle, the water matrix is allowed to elute from the column, and when the baseline of the instrumental response stabilizes, the temperature program is applied at the maximum permissible rate. The peak for cetyl alcohol appears at approximately 230°C.

Calibration. A series of standard solutions of cetyl alcohol is prepared by initially preparing a 100-ppm standard solution of cetyl alcohol in a water-isopropyl alcohol (3:1) matrix and diluting the standard solution to the required concentration levels with distilled water. Standard solutions of the required concentration levels are analyzed according to the procedure described above and a calibration curve is prepared from results of the analysis.

Calculations. The concentration of cetyl alcohol in water is determined by comparing the peak area obtained with the calibration curve.

Sensitivity. The experimentally demonstrated sensitivity of this procedure is 0.5-ppm cetyl alcohol in water. With an electrometer of better quality, two orders of magnitude increase in sensitivity might be expected.

ANALYSIS OF AMINES IN WATER

Desalination processes, based on solvent extraction, utilize secondary and tertiary amines with five and six carbon atoms. These amines have properties such as high vapor pressure, low density, and low viscosity, which facilitate extraction separation and solvent recovery. Because amines used in the process come in direct contact with water, methods for the detection of such materials in potable water are required. To develop such a method, a study has been conducted consisting of two parts: gas chromatographic separation and detection in a water matrix.

Separation

A number of conventional gas chromatographic columns were tried for the separation of a mixture of primary C_3 to C_7 amines. The best results were obtained on an Apiezon L substrate pretreated with KOH. The separation of amines was accomplished under the following set of conditions:

Instrument:	Aerograph HyFi Model 600C
Detector:	Flame ionization; hydrogen flow 25 cc/min; air flow 250 cc/min
Column:	3-foot long by 1/8-inch diameter packed with substrate containing 5-percent Apiezon L and 10-percent KOH on Chromosorb W 80-100 mesh

Carrier Gas:	Nitrogen, inlet pressure 20 psig
Sample:	2 μl of primary amines (C_3, C_4, C_5, C_6, C_7)
Temperature:	Programmed from 45° to 110°C
Sensitivity:	10 x 32
Recorder:	L&N, 1-millivolt, full-scale response; speed, 0.5 in./min

The chromatogram of amines is shown in Fig. 8. The retention times and elution temperatures are shown in Table 5.

Determination of Amines in a Water Matrix

Solutions containing varied concentrations (1 to 1000 ppm) of primary propyl amine in a water matrix were prepared and an attempt was made to analyze these solutions under gas chromatographic conditions as previously stated. Because of the high sensitivity of the instrument used for this work, column bleeding, characteristic of gas-liquid chromatography, seriously obscured the readout.

TABLE 5

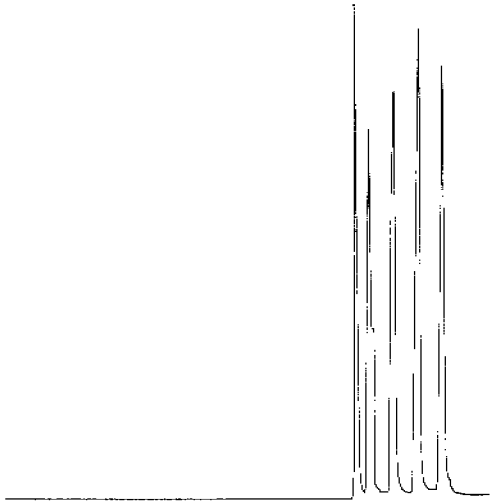
SEPARATION OF PRIMARY AMINES

Amine	Retention Time, minutes	Temperature of Elution, °C
$C_3H_7NH_2$	0.5	45
$C_4H_9NH_2$	1.0	55
$C_5H_{11}NH_2$	2.0	70
$C_6H_{13}NH_2$	3.0	90
$C_7H_{15}NH_2$	4.0	105

NOTE: Conditions of analysis reported in text

An attempt to elute amines from a porous glass column under normal operating conditions using inert gases as the carrier was unsuccessful. It was considered, however, that if the polarity effects of a porous glass column could be negated or reduced, amines could be eluted from such a column.

An attempt was made to reduce the polar effects of the porous glass substrate by the use of a polar carrier vapor, which competes with the amines for the polar sites on a column. Because of the higher polarity of water, it was used as a carrier vapor. A standard solution of propylamine was



Conditions		Peaks in order of elution		
		Component	Time	Temperature
Instrument:	Aerograph HyFi, Model 600 C	$C_3H_7NH_2$	0.5'	45° C
Detector:	Flame Ionization H_2 flow, 25 cc/min; air flow, 250 cc/min.	$C_4H_9NH_2$	1'	55° C
Column:	3-foot long, 1/8-inch-diameter packed with 10 percent KOH and 5 percent Apiezon L on 80-100 mesh Chromosorb W acid washed.	$C_5H_{11}NH_2$	2'	70° C
		$C_6H_{13}NH_2$	3'	90° C
Sample:	2 microliters of mixed amines.	$C_7H_{15}NH_2$	4'	105° C
Carrier Gas:	Nitrogen, inlet pressure 20 psig			
Temperature:	Programmed from 45° C to 110° C			
Sensitivity:	10 x 32 attenuation			
Recorder:	Leeds & Northrup Speedomax, 1mV full scale response, 1/2 in./min. chart speed.			

Figure 8. Separation of C_3 to C_7 Primary Amines

prepared and analyzed under temperature-programmed conditions on a porous glass column using water vapor as the carrier gas. It was found that this technique does facilitate removal of amines from a porous glass column at a fairly high temperature. It was established that to elute propyl amine from a 5-foot-long porous glass column, a temperature of 290°C must be maintained.

A number of standard solutions of propyl amine was prepared and analyzed using the direct gas chromatographic procedure. The results reported in Table 6 indicate that the average response of the instrumentation system (HyFi model 600C instrument) to 1 microgram of propyl amine equals 273 cm^2, which would permit detection of such materials in a water matrix at the ppb concentration level.

TABLE 6

DETECTION OF PROPYL AMINE IN A WATER MATRIX

Amine Concentration, ppm	Sample Size, μl	Micrograms of Amine Injected	Instrument Response, cm^2	Response, cm^2 per Microgram of Amine
1	10	0.01	2.7	270
10	5	0.05	11.1	220
10	10	0.10	32.9	329

NOTE: Wilkens HyFi Model 600C gas chromatograph was used. Average Response 273 cm^2/microgram of amine corrected for maximum sensitivity

While the developed technique permits detection of amines in water solutions at the required sensitivity levels, the efficiency of the separation is rather poor, and high temperatures are required to elute even low boiling members of the amine family. Nevertheless, the described technique provides the only known gas chromatographic approach to the solution of this problem.

It is possible by using this technique to determine the total amine content of the water samples, and the proposed procedure for the analysis of amines in a water matrix is intended to achieve that end.

Proposed Procedure for the Analysis of Amines in a Water Matrix

Instrumentation Requirements. A gas chromatograph is fitted with a porous glass column, flame ionization detector, and a steam generator to produce the carrier gas.

Procedure. The gas chromatograph is operated under the following set of conditions:

Detector:	Flame ionization; hydrogen flow, 25 cc/min; air flow, 250 cc/min
Column:	5 feet long, 1/8-inch diameter, packed with Corning Glass Co. porous glass No. 7930, 50-80 mesh size
Carrier Gas:	Steam, 12-psig inlet pressure
Temperature:	Starting at 290°C isothermal and programmed to 400°C if higher boiling amines are present in sample
Sample:	Amine in water

Calibration. A series of standard solutions is prepared by the dilution technique, and is analyzed according to the procedure described above. A calibration curve is prepared.

Calculations. The concentration of amines in a water sample is established by comparing the peak area obtained with the calibration curve.

Sensitivity. The technique is capable of detecting sub-ppm concentration of amines in water.

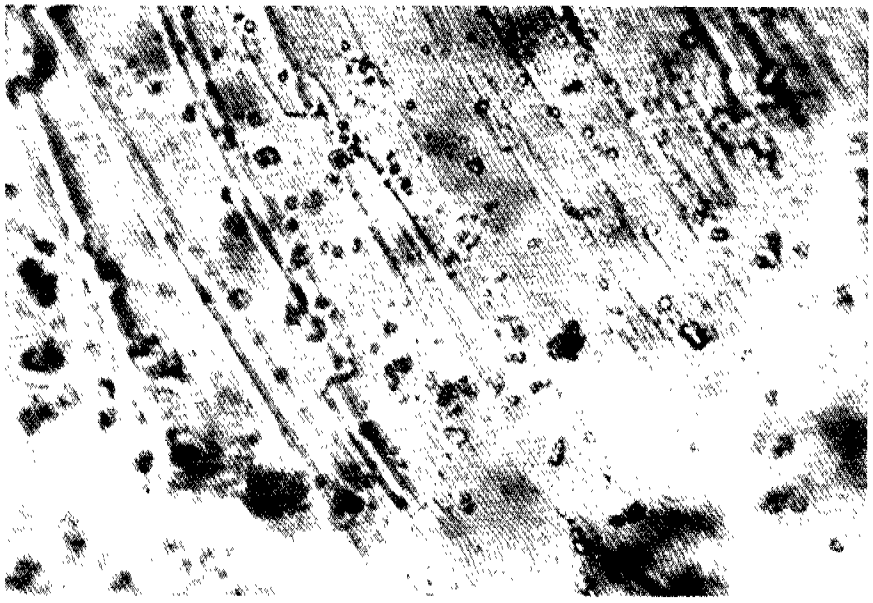
CHARACTERIZATION OF POROUS GLASS AS A GAS CHROMATOGRAPHIC SUBSTRATE

The polarity of porous glass precluded efficient use of this substrate for the separation of polar materials. The use of a water stream as a carrier did not resolve all of the problems of polarity.

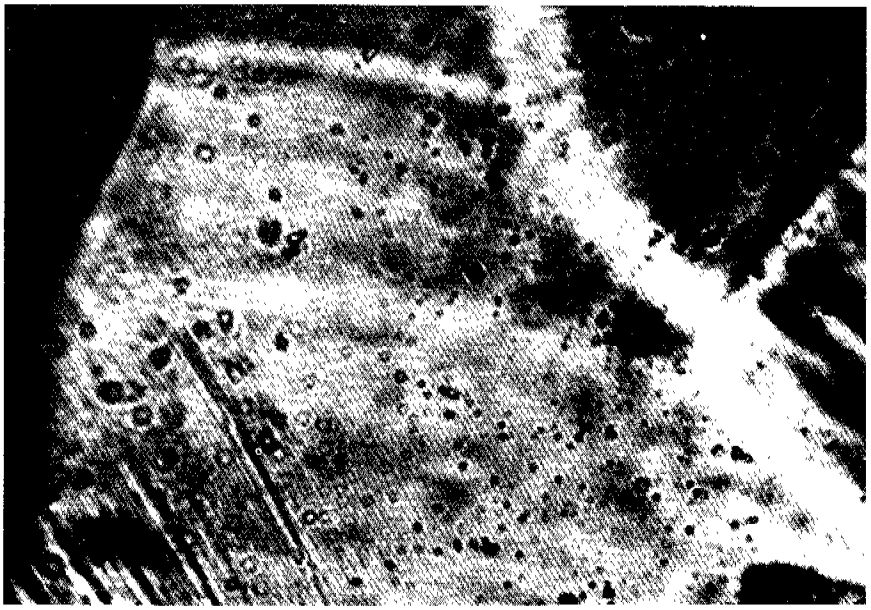
A study was initiated to modify the physical properties of porous glass to permit the separation of polar materials. The modification was achieved by the deposition of a thin layer of polymer on the porous glass grain. The physical characteristics of untreated and treated porous glass were then determined in order to establish a theoretical basis for future experimental approaches to the modification of this substrate.

Untreated Porous Glass

The starting material for the preparation of the column packing was porous glass, Code 7930, Corning Glass Co., New York. The material was reported to have a pore size of 40 Å. The plates of porous glass were ground and sieved. The 50-80 mesh size material was used in this study. A grain of porous glass was examined microscopically. A photograph of a portion of a grain surface at approximately X1200 magnification (X3.7 photographic and X320 microscopic) is shown in Fig. 9. An examination of this photograph indicates a number of fairly uniformly distributed pores, which also appear to be of uniform pore diameter. An extensive striation of the surface



(A)



(B)

Figure 9. Microscopic Photographs of Untreated (A) and Phenol-Formaldehyde Treated (B) Porous Glass Grain at X1200 Magnification

can be observed. The striation which manifests itself in a number of sharp ridges and cracks on the surface of a grain, was probably produced by a mechanical breakdown and abrasion of the fused glass during the grinding procedure. The surface area, pore volume, and pore size of the ground material were determined. A number of commonly used gas-solid chromatographic absorbants were also examined using the same procedure. Results are reported in Table 7. Porous glass has a considerably smaller surface area and a smaller pore volume in comparison with activated charcoal, silica gel, or alumina. Its pore size is slightly larger than the pore size of activated charcoal and silica gel and smaller than the pore size of alumina. A Carbon black, Raven 11 brand, produced by Columbia Carbon Co., has many of the same surface characteristics as porous glass.

TABLE 7

SURFACE CHARACTERISTICS OF SELECTED ADSORBANTS

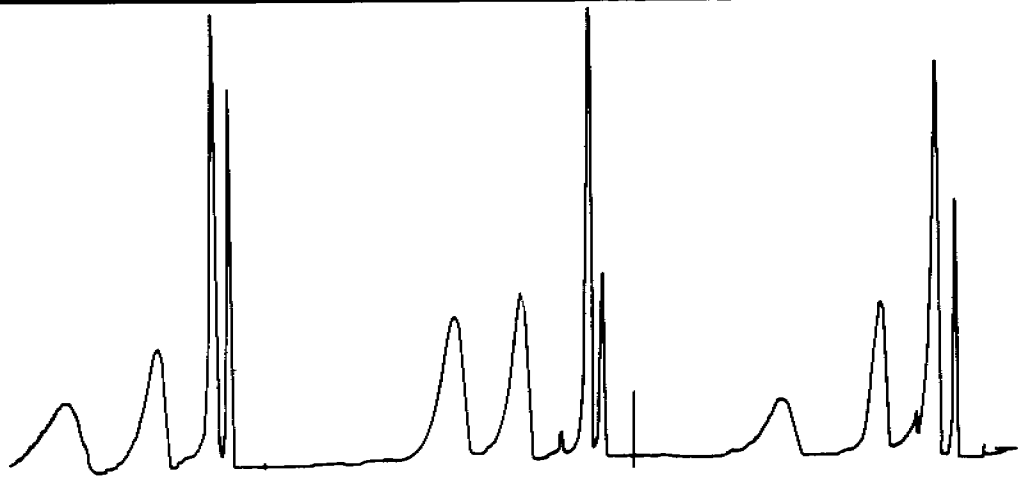
Adsorbants	Surface Area, m^2/gram	Pore Volume, ml/gram	Average Pore Size, Å
Porous glass of 50-80 mesh size	173.2	0.109	25.2
Porous glass coated with 0.6 percent w/w phenol-formaldehyde resin, 50-80 mesh size	146.5	0.097	26.5
Porous glass coated with 3.0 percent w/w phenol-formaldehyde resin, 50-80 mesh size	128.1	0.098	30.6
Carbon black, Raven 11, Columbia Carbon Co.	156.8	0.095	24.2
Activated charcoal, Col-L, Columbia Carbon Co.	1401.5	0.560	16.0
Silica gel, Davison SMR-55-1097-1	566.0	0.250	18.0
Alumina, Engelhard Industries, MFSS	251.0	0.280	44.0

Polymer-Coated Porous Glass

Substrates containing 0.6-percent w/w polymer and 3.0-percent w/w polymer were prepared in the following manner: a varnish of phenol-formaldehyde resin of approximately 60-percent total solids content was diluted in reagent-grade acetone. For the preparation of 0.6-percent w/w coating

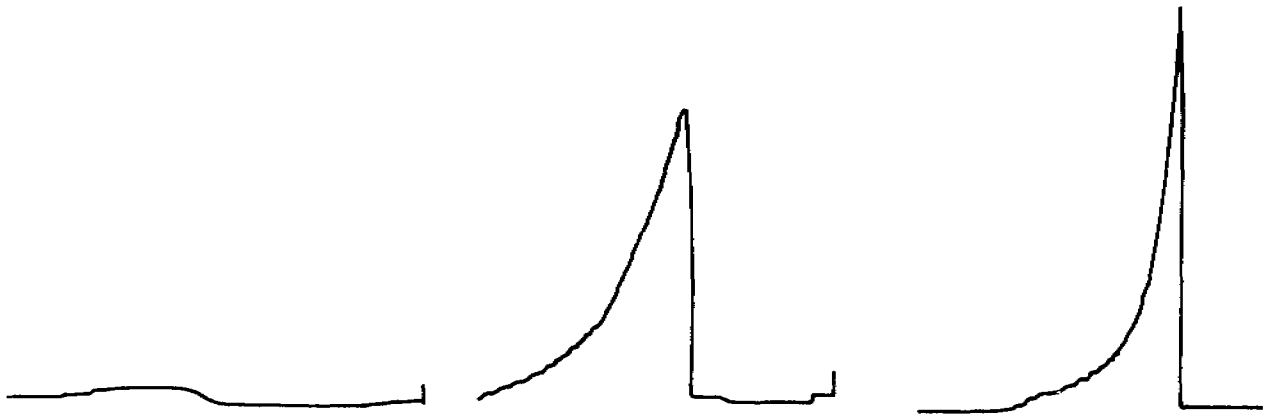
50 micrograms of the varnish (30 micrograms of the resin) were dissolved in 10 milliliters of acetone and combined with approximately 5 grams of porous glass previously dried at 400°C. For the preparation of 3.0-percent polymer coating, 0.25 gram of the varnish was used in the same manner. The acetone was evaporated at room temperature with constant mixing. The "dry" material was then packed into a 1/8-inch-OD tube and inserted in a gas chromatograph. The column was then purged with nitrogen gas for 30 minutes to remove the residual air and the remaining solvent. The column was slowly heated to 150°C under a nitrogen flow and left overnight at that temperature to complete the resin cure. The 3.0-percent polymer-coated porous glass was examined microscopically, and prints of the grain at X1200 magnification indicated a fairly uniform and consistent film of polymer across the surface of the particle (Fig. 9). The surface area, pore size, and pore volume of the polymer-modified substrates were determined and the data are presented in Table 7. As these data reveal, the polymer-modified porous glass surface area is reduced in comparison to the untreated material; however, the pore volume and the pore size are changed very little.

Figure 10 shows chromatograms of four Freons on treated and untreated porous glass materials. As the chromatograms indicate, the separation patterns are fairly similar on untreated, 0.6-percent w/w polymer and 3.0-percent w/w polymer-treated substrate in terms of retention times and peak symmetry. Because the adsorptive materials tested are similar in pore volumes and sizes, but different in surface area, it can be assumed that the mechanism of gas/solid chromatographic separation of nonpolar materials on ground porous glass is caused by pore adsorption. Figure 11 shows gas chromatograms of methanol on untreated porous glass and 0.6-percent polymer and 3.0-percent polymer-coated substrate. It is apparent that untreated porous glass adsorbs and nearly completely retains methanol; however, it elutes on polymer-treated substrates. The reason for a strong adsorption of polar materials on ground porous glass, therefore, must be caused by a phenomenon other than pore adsorption. The effect of this phenomenon can be overcome by deposition of a thin polymer film on porous glass grains.



Conditions		Peaks in order of elution
Instrument:	Aerograph HyFi, Model 600 C	Chlorotrifluoromethane
Detector:	Flame Ionization, H_2 flow, 20 cc/min; air flow, 250 cc/min.	1,1-Difluoroethylene
Columns:	(1) 6-foot long, 1/8-inch diameter packed with Corning Co. porous glass No. 7930, 50-80 mesh size. (2) 6-foot long, 1/8-inch diameter packed with Corning Co. porous glass No. 7930, coated with 0.6 percent phenolformaldehyde resin. 50-80 mesh size. (3) 6-foot long, 1/8-inch diameter packed with Corning Co. porous glass No. 7930, coated with 3.0 percent phenolformaldehyde resin. 50-80 mesh size.	Dichlorodifluoromethane Chlorodifluoromethane
Sample:	Mixture of Freons; sample size 40 microliters.	
Carrier Gas:	Nitrogen gas; inlet pressure 12.5 psig.	
Temperature:	50°C isothermal.	
Sensitivity:	Varied	
Recorder:	Varian, 9 mV full scale response, speed 2.5 minutes per inch	

Figure 10. Separation of Freon Mixture



Conditions	
Instrument:	Aerograph HyFi, Model 600C
Detector:	Flame Ionization; H_2 flow, 20 cc/min; air flow, 250 cc/min.
Column:	(1) 6-foot long by 1/8-inch diameter packed with Corning Co. porous glass No. 7930, coated with 3.0 percent phenolformaldehyde resin, 50-80 mesh size. (2) 6-foot long by 1/8-inch diameter, packed with Corning Co. porous glass No. 7930, coated with 0.6 percent phenolformaldehyde resin. 50-80 mesh size. (3) 6-foot long by 1/8-inch diameter, packed with Corning Co. porous glass No. 7930, 50-80 mesh size.
Sample:	Methanol, 0.5 microliter.
Carrier Gas:	Nitrogen Gas; inlet pressure 35 psig.
Temperature:	200° C Isothermal.
Sensitivity:	100 x 16
Recorder Speed:	Varian, 9 mV full scale response, speed 2.5 minutes per inch.

Figure 11. Gas Chromatograph of Methanol

PHASE 2: DETERMINATION OF THE CHEMICAL NATURE OF ORGANICS FOUND IN NATURAL WATER SOURCES

DEFINITION OF THE PROBLEM

The extremely low concentrations of specific organic materials present in natural water sources, combined with the existence of complex biological species, precludes their direct qualitative and quantitative analysis. The analysis for total organic matter in water is usually carried out after a preconcentration step. The standard analytical techniques used by water chemists involve adsorption of the organic matter, usually on activated charcoal, followed by elution with organic solvents. Such a procedure suffers from incomplete adsorption and/or desorption of the organic material, which becomes very acute with the determination of macromolecules. Frequently, the eluent introduces trace impurities which interfere in the subsequent analysis, especially if determinations at the parts/billion level are attempted. For these reasons, it is believed that preconcentration by adsorption is unsatisfactory when used as part of the procedure dealing with detection and identification of organics in natural water.

The concentration of naturally present organics in water varies, and is estimated to be in the sub-ppm concentration in potable water, 2 to 10 ppm in sea water, and considerably higher concentrations in sewage and brackish water. The analytical technique should be very sensitive and sufficiently versatile to analyze highly polluted water sources.

An analytical system capable of handling fairly large water samples has been designed. The principle is based on the removal of the volatile organics from the water by vacuum stripping. The volatile organics are then condensed in cold traps and the nonvolatile organics remain in the sample flask. The instrumentation system should accept water samples ranging from 2 to 250 milliliters.

APPARATUS

The apparatus is shown in Fig. 12 and the schematic is shown in Fig. 13. The essential components of the system are:

1. A specially designed sample flask (500 cc volume with three outlets) which permit vacuum transfer of the sample without disconnecting the flask (13*) from the system (Fig. 13)
2. A drying cartridge (12) with bypass (11)
3. An empty metal coil (14) with a bypass (15) for the collection of C_2 and higher organics
4. A two-way valve (10) serving the vacuum evacuation system and the on-stream gas chromatograph; the two-way valve is provided with two U-tubes, one packed with silica gel for the collection of methane, the other empty used for the transfer of C_2 and higher organics from the trapping loop prior to the injection in the gas chromatograph

*Numbers in parentheses refer to Fig. 13.

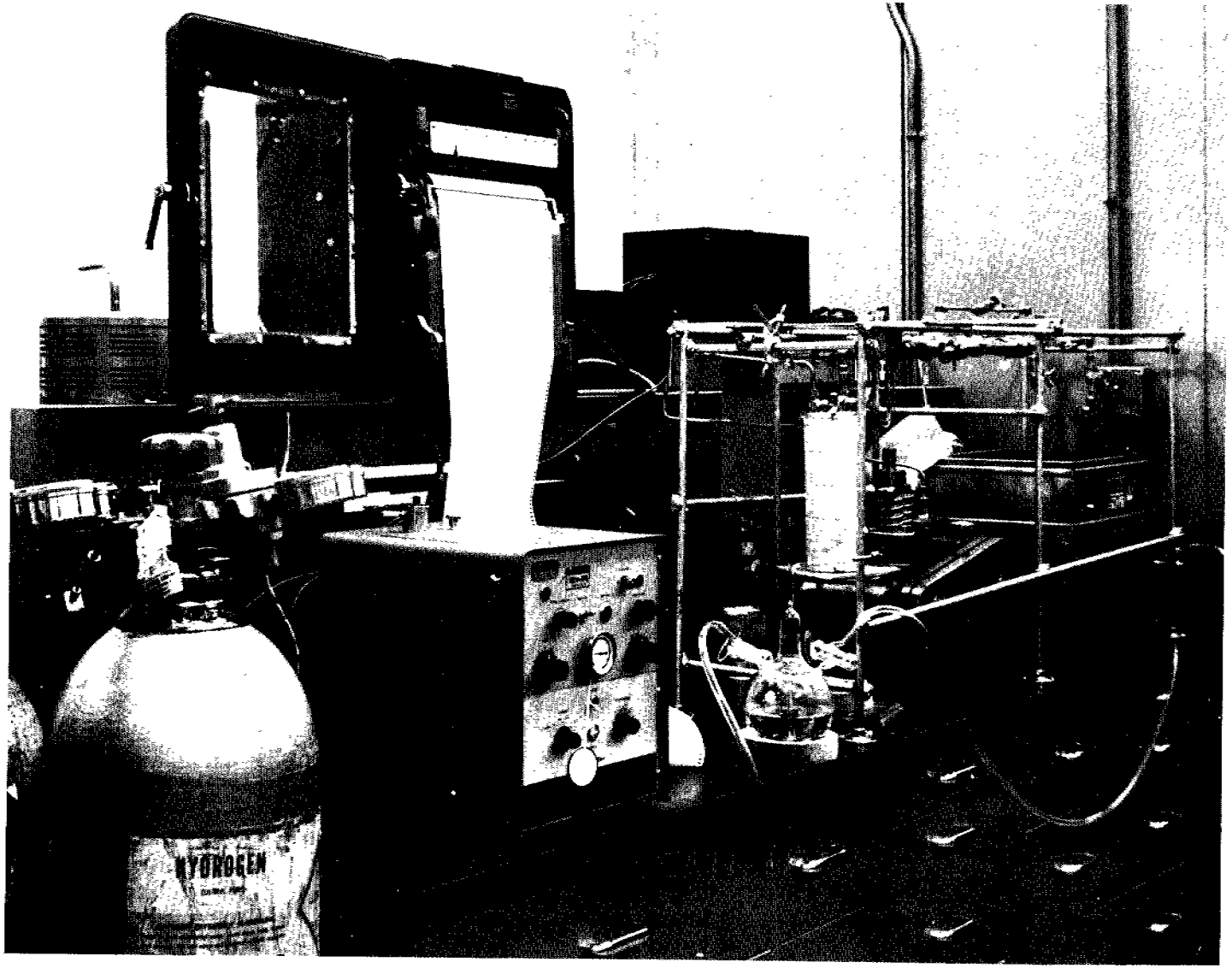
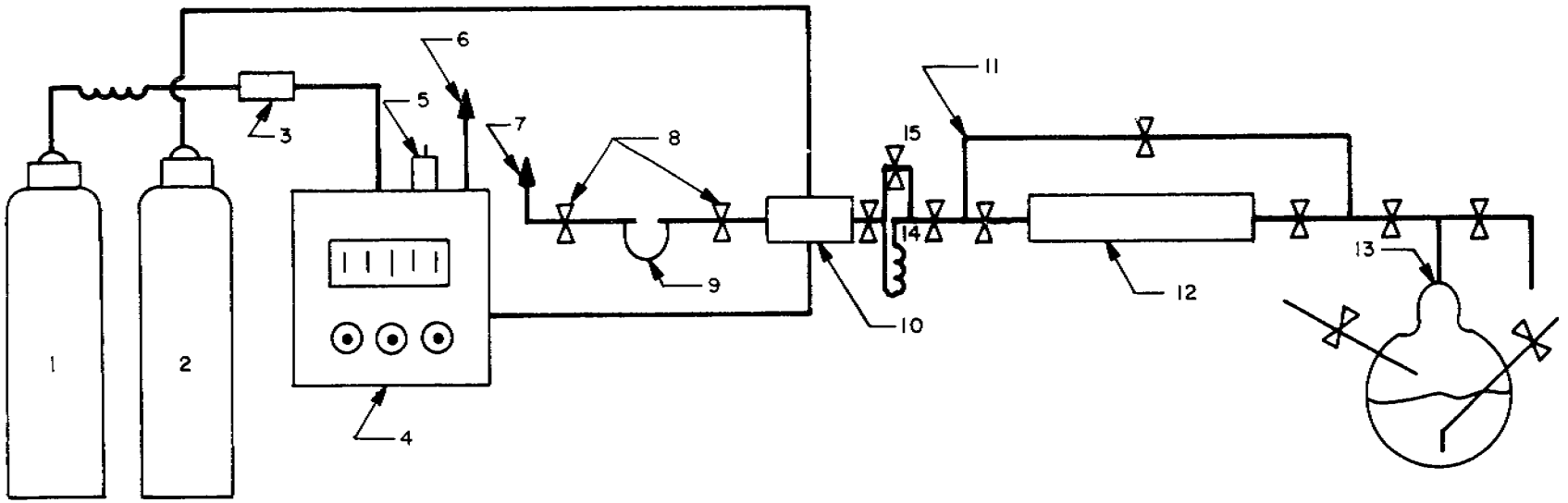


Figure 12. Test Setup for Analysis of Volatile Organics in Natural Waters



1. SOURCE OF IONIZING GAS
2. SOURCE OF CARRIER GAS
3. FLOWMETER
4. GAS CHROMATOGRAPH
5. FLAME IONIZATION DETECTOR
6. RECORDER INLET
7. VACUUM PUMP INLET
8. SHUT-OFF VALVES
9. LIQUID NITROGEN TRAP
10. BECKMAN 2-WAY VALVE (SAMPLE TRAP)
11. AND 15. BY-PASS LOOPS
12. SOLID ADSORPTION TRAP (WATER VAPOR)
13. SAMPLING VESSEL WITH GLASS TO METAL VACUUM SEAL
14. EMPTY LOOP TRAP

Figure 13. Flow Diagram for Analysis of Volatile Organics in Natural Waters

5. A gas chromatograph with flame ionization detection (4, 5, 6)
6. A vacuum pump
7. A constant-temperature bath

PROCEDURE

The apparatus is vacuum evacuated, a funnel is connected to one of the side arms of the sample flask, and 2 to 250 milliliters of the water sample are introduced by slowly cracking the stopcock. The bypasses (11) and (15) are closed, and liquid nitrogen is placed around the trap (14) and the loops of the Beckman valve (10). Pumping on the sample begins and is continued until all of the water is removed. The volatile organics starting with ethane are retained in the chilled empty trap (14), while the methane (if present) is retained on the silica gel in the chilled loop of the Beckman valve.

The Beckman valve (10) is then rotated, placing the silica gel-filled loop into a stream of carrier gas. The loop is then rapidly heated to facilitate removal of the methane from the silica gel. The vaporized sample then passes through the separating column and is detected and recorded. During the next step, the condensed organic material in the downstream trap is transferred to the Beckman sampling valve by chilling the valve with liquid nitrogen while warming the downstream trap with pumping.

The Beckman valve loop is then rotated into the stream of the carrier gas and, after warming, the material is analyzed. The analysis is performed using a gas chromatograph under the following set of conditions:

Instrument:	Aerograph 600C, Wilkens Co.
Detector:	Hydrogen flame ionization
Column:	6-feet long, 1/8-inch diameter, packed with 50-80 mesh size Corning Glass Co. porous glass No. 7930; column is satisfactory for analysis of nonpolar materials; however, for the detection of polar components such as alcohols, ketones, carboxylic acids, more conventional substrates, such as Carbowax 20M on Chromosorb W, must be used
Carrier Gas:	Helium, 3-psig inlet pressure
Temperature:	Varied
Sensitivity:	Varied
Recorder:	Leeds & Northrup, 10 millivolt full scale

RESULTS

Hydrocarbons

The above experimental procedure was used for the analysis of hydrocarbons in water. Magnesium perchlorate (anhydrone) was used as the drying agent. The procedure was tested using an aqueous solution of natural gas. The composition of the natural gas was found to be, by weight:

Methane, 81.2 percent
Ethane, 11.4 percent
Propane, 5.6 percent
Higher hydrocarbons, 1.8 percent

The standard aqueous solutions were prepared in the following manner: A large funnel was connected to the evacuated sample flask; 200 cc of distilled water were introduced into the funnel, leaving approximately 1 cc of air trapped in the stem of the funnel. A gas-tight Hamilton microsyringe was filled with natural gas and the syringe was submerged until the needle touched the air bubble.

A measured amount of gas was then transferred into the air bubble and was permitted to diffuse into the water sample. Subsequently, the water sample (including the air bubble) was sucked into the sample flask.

Three aliquots of natural gas, viz., 2, 5, and 10 microliters, were used, yielding aqueous mixtures of the following composition:

Gas	Standard Solution I, ppb	Standard Solution II, ppb	Standard Solution III, ppb
Methane	6.4	16.0	32.0
Ethane	0.9	2.2	4.4
Propane	0.5	1.2	2.4

The samples were analyzed according to the procedure described in the preceding section. It was unnecessary to remove the total quantity of water sample used, because prior work (Ref. 17) indicated that total removal of low hydrocarbons from the water sample is accomplished in less than 30 minutes under an efficient vacuum operation. A calibration curve for methane is shown in Fig. 14. The linearity of this curve is surprising, but attests to the remarkable linearity of the detector. The gas chromatogram for standard solution II is shown in Fig. 15.

Natural Water

Satisfactory calibration of the system using aqueous hydrocarbon solutions was obtained. Data on the quantitative removal of the hydrocarbon from

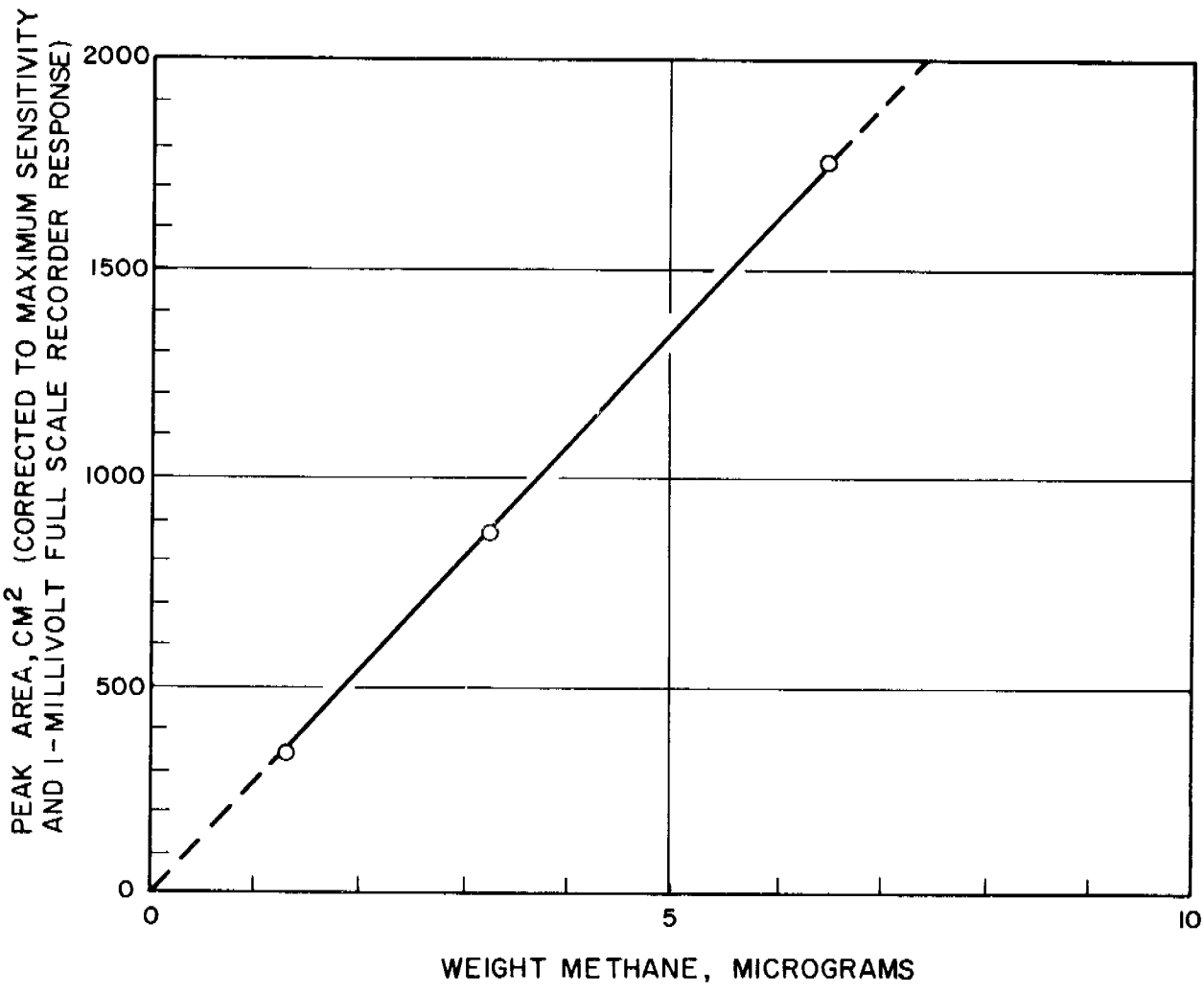
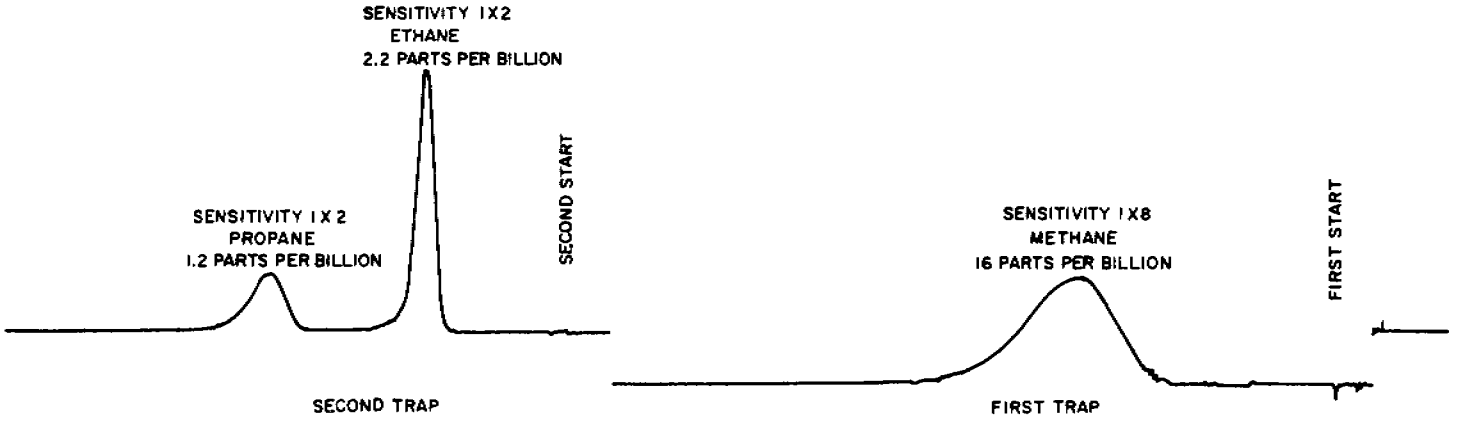


Figure 14. Methane Calibration



Conditions

Instrumental System and Procedure: As described in text.

Detector: Hydrogen Flame Ionization.

Sample: 200-cc distilled water containing 5 microliters of natural gas

Figure 15. Gas Chromatogram of Natural Gas in Water Solution

the water and the rates to effect this transfer were reported previously (Ref. 17). Because the method has now been developed, it remained to test the procedure on samples of water of unknown composition.

A number of fresh and sea water samples were collected in the Los Angeles, California area and were analyzed for volatile hydrocarbon content.

The results of these analyses are summarized in Table 8.

TABLE 8

VOLATILE HYDROCARBON CONTENT OF WATER SAMPLES

Water Sample	Hydrocarbon Found	Concentration, ppb
Los Angeles Municipal Water (Owens River)	Methane Ethane Propane	5 0.2 0.3
Rocketdyne Industrial Water	Methane	3.4
Spring Water (Los Angeles area)	None	-
Lake Arrowhead Water	Methane	3.1
Deep Well Water (Lake Arrowhead area)	None	-
Pacific Ocean Water (surf line)	Methane	0.09
Pacific Ocean Water (lagoon at Coral Beach)	Methane	0.9

Examination of Table 8 indicates that methane is the most common volatile hydrocarbon material detected in these natural water supplies. The data also suggest that methane concentrations are highest in water procured from supplies of higher biological activity and are absent in potable spring water and mountain deep-well water which, because of their purity, are used without chlorination. More experimental data will be required to draw valid conclusions, but indications are that the methane concentration in water supplies may be related to the biological organic activity, and might possibly be used as an index of biological purity.

DETECTION OF ALCOHOLS, KETONES, CARBOXYLIC ACIDS, AND AMINES IN WATER

The efficiency of the described system must be tested for the analysis of other classes of organic compounds which might be present in natural water sources.

The critical part of the procedure is the removal of the water matrix. The drying tube must be packed with chemically inert materials, and, at the same time, should not physically retain higher boiling compounds.

The initial experiments during this line of investigation were conducted using a methanol/water solution as the test substance and magnesium perchlorate as drying agent. It was discovered that the high heat of hydration had an adverse effect on the trace quantities of methanol. Drying agents such as phosphorus pentoxide and heavy metal oxides were rejected because of their reactivity towards alkaline or acidic materials. It appears that a mixed-bed absorption should be used; such a bed might comprise calcium sulfate and calcium chloride.

CONCLUSIONS

The results of this study demonstrated that the monitoring of product water using gas chromatographic techniques is feasible and practical.

The specific analytical techniques based on the common gas chromatographic methodology were developed for four classes of organic materials which are used in desalination processes: hydrocarbons, Freons, amines, and alcohols.

The developed techniques in all cases are capable of direct analysis of water samples, and have experimentally demonstrated the capability of detection in the sub-ppm concentration range.

A second phase of this program dealt with developing the methodology for the analysis of naturally occurring organics in water sources. An analytical approach based on separation and preconcentration by means of vacuum distillation of volatile and nonvolatile organic fractions coupled with removal of the water matrix appears to be feasible; however, fuller evaluation of this technique is indicated.

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